# STUDIES OF REACTION GEOMETRY IN OXIDATION AND
# REDUCTION OF THE ALKALINE SILVER ELECTRODE

## FOURTH QUARTERLY REPORT

Eliot A. Butler

Angus U. Blackham

May 15, 1969

J. P. L. 952268

Brigham Young University

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ABSTRACT

Cyclic current step measurements during the $Ag-Ag_2O$ oxidation
plateau have been made. The results of measurements are very
similar to those obtained from systems $(Ag-Ag(NH_3)_2^+, (Fe^{+2}-Fe^{+3})$
where the overvoltage is dependent on diffusion of an electro-
active species to the surface of an electrode. The exchange
current density, $i_o$, calculated from the relationship developed
by Wijnen and Smit[5] decreases from 1.44 $ma/cm^2$ to 0.75 $ma/cm^2$
along the $Ag-Ag_2O$ plateau.

The changes in the ohmic resistance of the silver oxide
film formed in 0.0543, 0.109, 1.09, 5.43, and 10.9 F KOH have
been measured. The maximum resistance of the oxide measured
in these electrolytes was 0.31, 0.28, 2.44, 5.15, and 0.16 $\Omega cm^2$.
Evidence for a proposed explanation of the changes which occur
in the oxide film resistance is presented. Experiments were
performed which show that two reduction reactions, $AgO-Ag_2O$ and
$Ag_2O-Ag$, proceed simultaneously at about equal rates during the
first reduction plateau until all of the AgO is reduced.

Charge acceptance by silver foil and wire electrodes as a
function of applied potential under potentiostatic conditions
has been measured. Three maxima are observed before oxygen
evolution. These occur at potentials of 0.34, 0.56, and 0.66
volt vs. Hg/HgO. At 0.66 v. an eleven-fold increase over the
charge acceptance at 0.56 was observed.

The effects of tension and torsion on the charge acceptance
of silver wire electrodes during the first oxidation plateau
have been studied. No increase or decrease in charge acceptance
was observed.

# S E C T I O N   I

## KINETIC STUDIES OF THE OXIDATION OF SILVER

## IN ALKALINE ELECTROLYTE

### Introduction

It was reported[1] that the high double layer capacitance of the
unoxidized silver electrode in KOH prevented cyclic current-step (c.c.s.)
measurements from being made on this system. However, once the oxide
film has formed, the double layer capacitance drops rapidly.[2,3].
Because of the decrease in capacitance after the oxide film forms,
c.c.s. measurements have been made during the $Ag-Ag_2O$ plateau. The
shape of the $\Delta\eta_\theta$ versus $1/\sqrt{f}$ curves obtained in the $Ag-Ag_2O$ system
is identical to the $\Delta\eta_\theta$ versus $1/\sqrt{f}$ curves obtained in the ferrous-
ferric and $Ag-Ag(NH_3)_2^+$ systems (compare the $\Delta\eta_\theta$ curves reported
here with those reported recently).[1] This shows that the concen-
trations of the rate controlling species behave as if they are
diffusion dependent. However, this alone is not sufficient evidence
to show a diffusion dependent reaction mechanism.

The study of the oxide film resistance has been continued. In a
previous report[1] the effect of electrode cycling and oxide thickness
on the ohmic resistance was presented. This report contains resist-
ance and charge acceptance measurements which were made in various
concentrations of KOH. An explanation of the oxide film resistance
data is proposed. The explanation considers the type of charge
carrier which is passing through the oxide film at any given time
and assumes that the ohmic resistance of the film to the passage of
electrons is much less than the ohmic resistance to the passage of
ions ($Ag^+$, $OH^-$, or $O^=$).

## Experimental

The modified apparatus for c.c.s. measurements is described in a previous report.[4] A further modification of this apparatus was made by using a calomel reference electrode and a Luggin capillary instead of the large counter electrode to measure the potential changes of the test electrode (see Figure 1). The c.c.s. measurements were made at various points along the $Ag-Ag_2O$ plateau during the oxidation of the silver electrode in KOH. In Figure 4 the points along the potential-time curve where the $i_o$ measurements were made are shown. To make the series of $i_o$ measurements shown in Figure 4 an electrode was oxidized with direct current to the first point, (2), indicated in Figure 4 (at 0.2 minutes). The d.c. was then interrupted and the emf of the test cell was balanced with the voltage divider so that an oxidizing current of less than $1\mu a$ was flowing. The c.c.s. measurements were then made as previously described[4] by observing the change in the magnitude of the peak-to-peak electrode voltage, $\Delta\eta_\theta$, caused by changing the square-wave frequency from 4-100 Hz. The results are presented as a plot of $\Delta\eta_\theta$ versus $1/\sqrt{f}$ (see Figure 3). When the c.c.s. measurements at the first point are complete the electrode is further oxidized to the second point and the procedure is repeated until the series of $i_o$ determinations during the $Ag-Ag_2O$ plateau shown in Figure 4 is finished.

The method for measuring the oxide film resistance was described in a previous report.[1] The temperature for all resistance and charge acceptance measurements was $25.0 \pm 0.1^o$ C.

The apparatus for the charge acceptance data is shown in Figure 2. Determinations of the ratio, r, (r is defined in the <u>Results and Discussion</u> Section) were made from the charge acceptance data as follows:

1. A silver foil electrode is oxidized to an arbitrary point on the second plateau where the constant current is interrupted and the electrode is removed from the cell. The amount of oxidation which has occurred at the potential of the second plateau up to this point is expressed as a percentage of the average second plateau length (see Figure 7).

2. The silver oxides are dissolved off the electrode with 0.5 F $NH_4OH$ and the total silver in the resulting solution is measured with a Perkin Elmer 303 atomic absorption spectrograph.

3. The value of r is then calculated from the equation given below.

$$\frac{I \ (eq. \ wt.)}{F} \ [a + (1 - r) \ b] = y$$

where y = mg of silver determined by atomic absorption

a = time in seconds for the first oxidation plateau

b = time in seconds of oxidation at the second plateau before the current is interrupted

I = direct current flow

F = Faraday constant

eq. wt. = equivalent weight of silver

This equation relates the experimentally measured total silver, y, to the coulometrically calculated total silver. The ratio r is included in the coulometric calculation to account for the amount of charge which goes to the formation of AgO or adsorbed atomic oxygen from $Ag_2O$.

## Results and Discussion

### Cyclic Current-Step Measurements

Cyclic current-step measurements expressed as a graph of electrode

voltage response $\Delta\eta_\theta$ versus $1/\sqrt{f}$ where f is the frequency, show a linear region which decreases rapidly at high frequencies. This rapid decrease is caused by the double layer capacitance of the electrode. As previously reported[1] the double layer capacitance on the unoxidized electrode is so high that no linear region with a positive intercept is obtained from c.c.s. measurements. As an oxide film forms, a linear region appears and the length of this linear region increases as the oxide film thickness increases. This is in accordance with results previously reported[2] and also with the findings of Cahan and coworkers[3] which show a large decrease in double layer capacitance as the $Ag_2O$ film forms. Thus the double layer capacitance will have less and less effect on the voltage response of the electrode as more oxide forms. Figure 3 shows that just before the second oxidation plateau is reached, the linear portion of the plot extends up to about 40 Hz, whereas near the beginning of the first plateau the plot is linear only to about 10 Hz.

The c.c.s. data for the $Ag-Ag_2O$ electrode (Figure 3) are similar to plots obtained by Wijnen and Smit[5] and also to our results[1] for systems in which the concentration of the electroactive species at the surface of the electrode is diffusion dependent. Although the theory of Wijnen and Smit[5] was based on a diffusion dependent model which may not apply to the case of an oxide covered electrode, for purposes of comparison the data reported here will be reported in terms of $i_o$ values calculated from their derived relationship:

$$i_o = \frac{RT\ i_A}{nF\Delta\eta_\theta}$$

where $i_A$ is the square wave current density, $\Delta\eta_\theta$ is the measured

voltage response of the working electrode, and R, T, n, and F have their usual electrochemical significance. The data in Table 1 show a decrease in $i_o$ values from 1.44 to 0.75 ma/cm$^2$ with time of oxidation along the Ag-Ag$_2$O plateau. A value of 2 ma/cm$^2$ was obtained by Dirske[7] from a single pulse method.

A plot of $i_o$ versus time is shown in Figure 4. Before a simple functional relationship between $i_o$ and time can be shown, the effect of current interruption on the plateau length must be overcome. Each interruption of the d.c. oxidation in order to make a c.c.s. measurement tends to lengthen the first plateau at the expense of the second plateau.

As mentioned above, the equations developed by Wijnen and Smit[6] are based on the well established model which relates the electrode overpotential to diffusion of the electroactive species. The fact that the experimental plots resemble those from systems for which the theory applies is evidence of diffusion dependence. Experiments performed by Dirkse and De Roos[12] indicate that the formation of Ag$_2$O is controlled by OH$^-$ diffusion. Therefore, if a reaction of the type

$$2Ag + 2OH^- = Ag_2O + H_2O + 2e^-$$
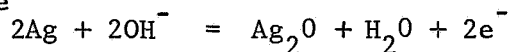
is taking place at the surface of the electrode, then the electrode overvoltage may be dependent upon the diffusion of the OH$^-$ ions. If, however, the concentration of the electroactive species involved in the rate controlling step of the reaction is not dependent on diffusion from the bulk electrolyte, then the equations of Wijnen and Smit should not apply. In this case a theory based on another model would have to be developed which may give $\Delta\eta_\theta$ a different functional relationship with frequency.

Measurements of Oxide Film Resistance

The resistance changes which occur during the oxidation of silver in 1.09 F KOH have been reported.[1] It was pointed out that it is difficult to measure accurately the magnitude of the resistance peak which occurs during the transition from the $Ag-Ag_2O$ to the $Ag_2O-AgO$ plateau. This is because of the large and rapid changes in the magnitude and shape of the oscilloscope waveform during this transition. Cahan and coworkers[3] also reported similar difficulties in measuring the resistance peak during this transition.

A resistance curve for the reduction of a fully charged silver electrode (in 1.09 F KOH) is shown in Figure 5. Because of the effect of KOH concentration on charge acceptance[8] it was expected that the resistance-time curves would also show a concentration dependence. Resistance-time curves were measured during the oxidation and reduction of silver in KOH solutions of 0.0543 F to 10.9 F. The resistance-time curves (the time scale is normalized to an arbitrary potential-time curve) obtained in these KOH solutions are compared in Figure 6. The maximum resistances measured during the $Ag_2O-AgO$ plateau for each KOH concentration are compared with the total charging times (3.57 $ma/cm^2$ constant current charging) in Table 2. Included in Table 2 are the results reported previously[1] which show the effect of cycling on the resistance. In each case an increase in charge acceptance caused by KOH concentration changes or by cycling is reflected by an increase in oxide film resistance.

Cahan and coworkers[3] explained the rapid rise in the resistance which occurs at the end of the first oxidation plateau as the result of the change from an electrode which is partially covered by the oxide film to one which is completely covered. The subsequent fall

in resistance was explained in terms of the higher conductivity of
the AgO. The electron diffraction, electron microscopy, and X-ray
studies performed by Thirsk and coworkers[10] indicate that complete
coverage of the electrode occurs early in the first plateau. Therefore,
an explanation is required which depends upon factors other than
incomplete coverage by the oxide film. A possible approach is to
consider the passage of charge carriers ($Ag^+$, $OH^-$, $O^=$, or $e^-$) through
a primary $Ag_2O$ layer of 50-100 Å consisting of randomly oriented,
small crystals.[10] If the mechanism for silver oxidation fits the
theory developed by Mott[13] for the formation of oxide films in which
the resistance to the passage of ions is much greater than the
resistance to the passage of electrons, then the changes in the
resistance during an oxidation-reduction cycle can be explained.
An explanation which we are considering is discussed below.

During the first plateau, ions must pass through an $Ag_2O$
layer of increasing thickness. The resistance and potential
must rise. When the potential is high enough, nucleation of
AgO can occur and the $Ag_2O$-AgO reaction begins at the
electrolyte-$Ag_2O$ interface.[11] At this point most of the
current flow through the $Ag_2O$ film is carried by electrons
released by the surface reaction

$$Ag_2O + 2OH^- = 2AgO + H_2O + 2\ e^-$$
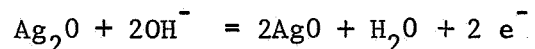
and a decrease in ohmic resistance results. The resistance
increases as the AgO deposit builds up and $O^=$ or $OH^-$ are the
charge carriers through the increasing thickness of AgO.
About 60% of the way along the AgO plateau (in 1.09 F KOH)

the resistance begins to decrease and a slow rise in electrode potential is noted. These results suggest the beginning of another reaction at the electrolyte-electrode interface such as

$$2OH^- = O_{adsorbed} + H_2O + 2e^-$$

where less and less of the total current-flow through the underlying oxide is carried by ions. This is consistent with the observation that the oxide film resistance is low at the oxygen evolution potential where the current-flow through the oxide film is carried by electrons which result from the oxygen producing surface reaction.

If the above model is acceptable, we should be able to measure the following:

1. A significant increase in the ratio, r, towards the end of the second oxidation plateau, where

$$r = Q_H / Q_{total} \qquad \text{and}$$

$Q_H$ = the quantity of charge which flows during the second oxidation plateau for the formation of AgO or adsorbed atomic oxygen.

$Q_{total}$ = the total charge which flows during the second oxidation plateau.

An increase in the ratio would indicate the beginning of a surface reaction forming atomic oxygen or related species. The occurrence of a new surface reaction would lead to the decrease in the oxide film resistance which occurs about 60% of the way along the second plateau (see Figure 6).

2. The formation of nine times as much AgO in 1.09 F KOH as in 0.109 F KOH because the maximum oxide film resistance measured during the second oxidation plateau in 1.09 F KOH is about 9 times

greater than that for an electrode oxidized in 0.109 F KOH (see

Table 2). The proposed model suggests that the resistance results

from the hindered passage of ions ($OH^-$ or $O^=$) through a nine times

thicker AgO layer. The experimental determination of r and the

9 fold difference in AgO formation are discussed below.

## Determination of the Ratio, r

The method for determining the ratio, r, was outlined in the

experimental section. Each r value is plotted against the

percentage of the second oxidation plateau (see Figure 7). This

percentage shows how far along the second plateau the oxidation had

proceeded before the current was interrupted and the electrode

removed. An r value plotted at 100% means that the oxidation of

the electrode was allowed to proceed to the end of the second

plateau where the potential rises to the $O_2$ evolution plateau.

Lower percentages indicate the length of the interrupted second

plateau compared to an average complete second plateau length.

The results of the r determinations in 1.09 and 0.10 F KOH are shown

in Figures 7A, B, and C. The curves in Figures 7B and C were

obtained in oxygen free electrolyte which was changed between runs.

The data in Figure 7A were obtained in the same manner except that

the electrolyte was not changed between runs. The difference could

be caused by small amounts of silver ion present in the electrolyte

from the solubility of silver oxide in KOH. The important fact

is that all three curves show a significant rise in r between 60

and 100% of the second plateau. Thus, associated with the decrease

in oxide film resistance which occurs in the latter portion of the

second oxidation plateau (in 1.09 F KOH) is an increase in the ratio r.

This increase in r suggests the beginning of a third reaction (such

as atomic oxygen formation at the electrode surface) about 60% of the way along the second plateau.

## AgO Charge Acceptance Data

Our experimental data show that the charge acceptance during the second plateau in 1.09 F KOH is about 3 times greater than in 0.109 F KOH. Comparison of Figures 7B and 7C shows that the ratio, r, at 60% of the second plateau is 2-4 times greater in 1.09 F KOH. Therefore, the total amount of AgO formed in 1.09 F KOH is 6-12 times greater than in 0.109 F KOH because a greater amount (2-4 times) of the 3 fold larger second plateau charge acceptance goes to the formation of AgO. The observation that 6-12 times more AgO is formed in the 1.09 F KOH supports the view that the 9 fold increase in oxide resistance measured in the 1.09 F KOH is caused by the greater amount of AgO formed.

In addition to making measurements of the ratio, r, during the second oxidation plateau, we made a similar set of measurements of r' during the first reduction plateau (in 1.09 F KOH).

$$r' = Q'_H / Q'_{total}$$

$Q'_H$ = the quantity of charge which flows during the first reduction plateau for the reduction of AgO to $Ag_2O$

$Q'_{total}$ = the total charge which flows during the first reduction plateau

The determination of r' is made in a similar manner to the determination of r (see Experimental section). For the determination of r' the electrode is first oxidized to the oxygen evolution plateau and then it is reduced to a preselected point along the first reduction at which time the current is interrupted and the electrode is removed from the cell and the silver oxides dissolved in 0.5 F $NH_4OH$. The

parameter, c, in the equation below is the time from the beginning

of reduction to the point where the current was interrupted. The

first of the three terms on the left side of the equation is the

weight of silver oxidized to $Ag_2O$ during the first oxidation plateau.

The second term is the weight of silver oxidized to $Ag_2O$ during the

second oxidation plateau. (Oxidation of $Ag_2O$ to $AgO$ does not, of

course, increase the weight of silver which is present as an oxide).

The third term is the weight of silver reduced from the oxide to

the metallic state during the first reduction plateau. The algebraic

sum of these terms is the weight of silver, y, present as the oxide

at the point of current interruption. This silver oxide is dissolved

from the electrode in ammonia solution and determined by atomic absorption.

$$\frac{I \ (eq. \ wt.)}{F} \ \left[ a + (1-r_{100})b - (1-r')c \right] = y$$

c = the time in seconds for the first reduction plateau

$r_{100}$ = the ratio, r, at 100%

a, b, y were previously defined

The value of r' is $0.45 \pm 0.13$ during the first reduction plateau

in 1.09 F KOH at 1.5 $ma/cm^2$. The data also show that the reduction

of AgO at the end of the first reduction plateau is complete.

Therefore, two reduction reactions $AgO-Ag_2O$ proceed simultaneously

at about equal rates (r' = 0.5) during the first reduction plateau

until all of the AgO is consumed. When all of the AgO is reduced,

the potential then drops to the second reduction plateau.

S E C T I O N  II

SURFACE AREA ESTIMATION

## Introduction

This section of the report deals with the development of methods

for the estimation of the effective electrolytic surface area of

rough and porous silver electrodes.  Two approaches to the problem

have been used.  The first is the estimation of the effective

surface area from data obtained from constant current oxidations.

This method is based on the assumption that oxidations at equal

current densities have equal depths of penetration of the silver in

forming the oxide layer.  This assumption allows calculation of the

effective surface area from data obtained from the comparison of

oxidations of smooth electrodes of known area to oxidations of

electrodes of unknown surface area.[2]  The second approach used is

the estimation of the effective electrolytic surface area from data

obtained from oxidations at constant potential, i.e., potentiostatic

oxidations.  Here the assumption is made that at oxidations at

equal applied potential the total charge acceptance per unit area will

be equal.  Based on this assumption a comparison of the total charge

acceptance per unit area of a smooth electrode of known area to the

total charge acceptance of an electrode of unknown area yields data

for calculation of the effective surface area of the unknown electrode.[4]

A comparison of the results of the two methods, given in a previous

report,[1] showed that the potentiostatic runs yielded higher values

for effective surface areas than did the constant current runs.  The

agreement was particularly poor for the porous sintered silver

electrodes with the potentiostatic experiments giving results about

20% higher.  The work of Wales and Simon has indicated that at constant

current the depth of oxidation varies with particle size and shape.[15]

These factors have prompted (1) further studies of the charge acceptance of silver electrodes under potentiostatic conditions and (2) a study of the oxidation of silver in the pores of a model porous electrode.

## Experimental

All potentiostatic oxidations were carried out in 0.1 N KOH solution which had been saturated in $Ag_2O$ to prevent dissolution of the oxide film. The runs were made at $20.0 \pm 0.1^{\circ}C$. Three types of electrodes were used: (1) vapor deposited film electrodes; (2) silver discs of 1.26 cm diameter punched from silver foil 0.051 cm thick; (3) silver wire of 0.49 mm diameter. The foil and wire electrodes were cleaned with abrasive cleanser and rinsed in distilled water and then KOH solution. They were then oxidized immediately to avoid surface contamination. The length of the wire that was oxidized was measured after each run in order to calculate the surface area of the wire involved in the reaction.

The current and the integral of the current vs. time were simultaneously recorded for all potentiostatic oxidations. The circuitry used in obtaining these recordings is given in Figure 11 of the second quarterly report.[14] The integral of the current vs. time gave the total charge acceptance. Immediately after some of these potentiostatic oxidations, reductions at constant current were made as a check on the total charge acceptance. These reductions were made at the same temperature and in the same electrolyte as were the potentiostatic oxidations. All reductions were made at a constant current of 1.000 $\pm$ 0.001 ma.

The extent of the oxidation under potentiostatic conditions was

determined by the amount of time required for the current to drop to a constant background current, on the order of 40 $\mu$ amps/cm.$^2$

For the study of the oxidation of silver within pores, a model porous electrode consisting of a bundle of silver wires in a glass capillary was constructed as shown in Figure 15.(a).

Electrical connection (A) was made through a serum cap (B). A 0.1 F KOH solution was forced by gravity flow to pass through arm (C). A thick walled capillary (D) with a base of 1.5 mm contained a bundle of seven silver wires. Each wire was 0.5 mm in diameter and 7 cm long. An enlarged end view of the silver wires and capillary tube is shown in Figure 15(b). The glass capillary was calibrated with etched divisions at 2 mm separation on its surface.

## Results and Discussion

The total charge acceptance as a function of applied potential for silver electrodes is given in Figure 8 and Table 3. In the discussion which follows five regions--I to V--of Figure 8 are considered. Graphs, of current vs. time, typical of each region of charge acceptance are given in Figures 9 to 14. Considerable differences in the shapes of these graphs, in the times to reach the background current, and in the magnitudes of the current are observed.

The first measurable oxide formation occurs at approximately 0.27 volt versus the Hg-HgO reference electrode. As the potential is increased from this value to 0.335 volts an increase in charge acceptance to 145 mcoul/cm$^2$ is observed as indicated in region I of Figure 8.

Fleischmann and Thirsk[10] have reported that a thin silver oxide

film of small randomly oriented crystallites is formed under conditions similar to those of region I here. They suggest that this film controls the rate of reaction and the extent of charge acceptance.

As the potential is increased from 0.335 to 0.400 volt the charge acceptance decreases from 145 to 65 mcoul/cm$^2$ as indicated in region II. The comparison of Figure 9 with Figure 10 shows that the current is higher initially at the higher potential but the time required to reach the background current is much less. Therefore, the total charge accepted (the area under the current-time curve) is smaller at the higher potential. Since the rate and extent of the reaction are controlled by the initial oxide film, it seems possible that the higher potential has produced a thicker film.[10] This allows rapid growth of oxide at first, on the surface of the film, but as a greater current density is forced to flow through this film the resistance to current flow increases much more quickly. At the lower potential the initial film is not as thick, and growth on the surface of the film may continue for a longer period of time, resulting in more change acceptance per unit area. Analysis of the current-time plots in light of this suggested model is not yet complete.

As indicated in region III of Figure 8 the increase of potential from 0.400 to 0.554 volt results in the charge acceptance increasing from 65 to 130 mcoul/cm$^2$. The next increase of potential, to 0.560 volt, results in an almost four-fold increase in charge acceptance, 486 mcoul/cm$^2$. After this second maximum the charge acceptance decreases to 70 mcoul/cm$^2$ with a further increase of potential to

0.610 volt shown as region IV of Figure 8. The current-time curves
in Figures 11 and 12 show the changes in this region. Figure 11 shows
an increase in the rate of the reaction after a short period of time
and then a decrease to the background current. This second current
peak appears earlier in the reaction at higher potentials, Figure 12.
The second current peak grows in magnitude with increased potential
until at 0.6606 it is greater than the first current peak, Figure 13.
At the evolution of oxygen, Figure 14, the first and second peaks
are so close together that they appear to be one peak on the time
scale at which the current-time plots were recorded.

Several runs were made at the potential given in Figure 12.
The reaction was interrupted at points A, B, C and D and the sur-
face of the electrode was examined. At point A the surface had a
thin brown film as was seen in the oxidations at lower potentials.
At point B a ring of black oxide had formed at the edge of the
electrode. At point C this black oxide ring had grown in toward
the center of the electrode. At point D the surface of the
electrode was completely covered with this black oxide. The
brown color is characteristic of $Ag_2O$ and the black color
characteristic of AgO.

Comparison was made of values for charge acceptance in this
region measured by a) integration of the current-time plots and
b) reduction at constant current. The results are given in
Table 4. These values agree best in oxidations which required
a relatively short time to reach the background current. The
KOH solutions used were saturated with $Ag_2O$ to inhibit dissolution
of the oxide.

At this time we do not have sufficient data to suggest whether relatively more of the oxide dissolves at the longer times or whether some internal adjustments are occurring within the reaction layer.

In region V at the potential 0.636 volt the charge acceptance increased to 100 mcoul/cm$^2$. At the potential 0.6606 volt the background current was not reached even after three hours, at which time the electrode showed a charge acceptance of 5557 mcoul/cm$^2$. This is more than an eleven-fold increase over the charge acceptance observed at the second maximum (486 mcoul/cm$^2$). As shown in Figure 13 this large charge acceptance is accompanied by a third current maximum. The second current maximum corresponded to the formation of AgO. This third maximum may also be associated with an oxide formation. As the potential is increased the maximum grows in magnitude just as did the AgO current maximum. The evolution of oxygen, however, limits its growth, Figure 14.

This large charge acceptance in a rather narrow potential range without oxygen evolution may have important implications in the improvement of cells using the silver-silver oxide electrode. We plan to determine the limits of this potential region and the extent of oxidation of silver electrodes in this region.

Oxidation of a Model Porous Electrode

Preliminary experiments have been made with the model porous electrode; constant current oxidations were made at currents from 160 to 240 $\mu$amps. Visual observations were made of the electrode during the oxidations, and the voltages were recorded continuously. Figure 16 is a plot of the potential-time curve

obtained with the model porous electrode at 160 μamp applied current. When the current is first applied the voltage rapidly rises (region A) and a very thin brown film is observed to cover the surface of the silver wires deep into the capillary (at least 2 cm). In region B the current increases linearly with time and a dark brown oxide (Ag$_2$O) grows longitudinally into the pore. The linear increase in the voltage is probably caused by the increase in electrolyte resistance as the reaction proceeds deeper into the pore. There was no observable change in region C. The linear region D is characterized by further growth of the dark brown and the appearance of a black oxide (AgO) at the open end. This black oxide grows into the pore. The black oxide is not visually apparent during the first minute or so of region D. The brown and black oxides appear to grow at the same rate. The maximum depths reached into the pores by Ag$_2$O and AgO were about 10 mm and 4 mm by the time of oxygen evolution. In region E the evolution of oxygen is clearly evident.

S E C T I O N   III

THE EFFECTS OF APPLIED STRESSES

ON THE OXIDATION OF SILVER

## Introduction

In the last quarterly report we described an experiment to det-

ermine the effect of tension on charge acceptance.[1]  Initial data

which we reported indicated little if any effect but the results were

somewhat uncertain because, 1) various current densities were used

and, 2) the charge acceptance during a given cycle appeared to be

dependent upon how far into the second oxidation plateau the previous

cycle has been allowed to proceed.

In this report the effect of an oxidation past the first oxidation

plateau upon subsequent cycles is described and conclusive results

of the effect of tension on charge acceptance are presented.

The effect of torsion on charge acceptance is reported.

## Experimental

The apparatus used in the tension experiments is the same as

that described in the third quarterly report.[1]  This apparatus was

modified for the study of the effect of torsion by fastening the top of

the silver wire electrode to a swivel instead of to a stationary beam.

This allowed the wire to be twisted any amount up to the breaking

point of the wire.  The wire was clamped just below the cell to limit

the torsion to the part of the wire in the cell and above the cell.

A two pound weight was applied to the electrode to keep it straight

and centered in the cell during reaction.

A current density of 1.0 mamp/cm$^2$ was used for all experiments.

The electrolyte used was 0.1 M KOH thermostatted to $20.0^{\circ}$C and

was renewed just prior to beginning the cycling of a fresh electrode.

The electrodes were prepared by cleaning with abrasive cleanser and

etching with 6 M $HNO_3$ for 5 to 10 seconds.[1]  This method of cleaning

does not give reproducible surface areas but does insure that the

surface is clean and will react uniformly. The comparison of

plateau lengths with and without tension (or torsion) is made from

data collected from experiments with the same electrode. Therefore,

the absolute surface area is not important as long as that surface

area does not change as a result of dirty areas beginning to react

in the course of the experiment. For this reason the initial

length of the first oxidation plateau, $C_1$, will vary from one set

of data to another. Similarly the slope of the curve of $C_1$ vs.

run number will vary. Any effect of tension (or torsion) on charge

acceptance, however, will appear as a break in the curve.

## Results and Conclusions

### The Effect of Tension on Charge Acceptance

The study of tension which was reported in the third quarterly

report has been concluded.[1]  Silver wire electrodes were cycled

by repeated oxidation to the end of the first plateau and reduction

to the evolution of hydrogen. Figure 17 a)shows the effects of cycling

a fresh electrode 60 times before applying tension. Run numbers

17, 30 and 33 were allowed to oxidize to the evolution of oxygen.

Runs 18, 31 and 34 (the subsequent oxidations) show the large,

temporary increases in first oxidation plateau lengths which we

reported previously.[1]    Within three or four cycles after this

oxidation to the evolution of oxygen the first plateau lengths

again returned to the predicted values.    The slope of the curve

shows an average increase in $C_1$ of 0.02 minutes per cycle.

The wire electrode was cycled 60 times without tension and

then progressively more tension was applied.  Four cycles at each

value of tension were run, followed by two cycles without weights.

These groups are shown in Figure 17 b) for 2, 4, 5, 6, 7 and 7.5 pounds..

The wire broke during the first oxidation cycle at 7.5 pounds.  No

increase or decrease is demonstrated by cycling under tension.

Breaks in the curve caused by oxidation of the electrode

beyond $C_1$ were avoided by our using freshly cleaned electrodes and

allowing no cycle to proceed more than five seconds into the

second oxidation plateau.  The first 25 cycles were made without

applied tension and then weights were added as before.  Figure 17 b)

is a graph of the results.  Again no increase or decrease resulted

from the tension.  Elongation was pronounced for electrodes which

had been subjected to 7 pounds of tension.


The Effect of Torsion on Charge Acceptance

Wire electrodes were cycled with a constant tension to demon-

strate the effect torsion has on charge acceptance.  The first 15

cycles were run with no torsion and then the electrode was cycled

3 times each with 0.5, 1, 2, 3, 4.5, 6.5, and 8.5 turns.  The

length of $C_1$ for each cycle is plotted in Figure 18.  Torsion was

not found to have any effect on the charge acceptance during $C_1$

even though noticeable deformation of the wire was caused by the

twisting.

When the electrode was released after being cycled at 8.5 turns it unwound only one turn. This shows that the twisting force produced a large amount of permanent deformation or shear and only a small amount of true torsion under the conditions of our experiment.

## Summary

We conclude from our experiments with tension and torsion that the charge acceptance of silver wire does not increase or decrease as a result of applied tension or torsion during the first oxidation plateau of the oxidation-reduction cycle.

TABLE 1

Data Obtained by Cyclic Current-Step (C.C.S.) Method from Figure 3.

Square Wave Peak to Peak Current Density = 1.26 ma/cm$^2$, d.c

Oxidizing Current Density = 3.1 ma/cm$^2$. Temperature 25$^\circ$C.

Total First Plateau Length = 2.44 min.

| Run Number | Time Along First Oxidation Plateau | Intercept | $i_o$ (ma/cm$^2$) |
|---|---|---|---|
| 1 | 0.00 | -14 mv | --- |
| 2 | .19 | 31.0 mv | 1.44 |
| 3 | .47 | 34.0 mv | 1.33 |
| 4 | .77 | 37.2 mv | 1.21 |
| 5 | 1.06 | 43.5 mv | 1.04 |
| 6 | 1.37 | 46.2 mv | .98 |
| 7 | 1.67 | 48.2 mv | .94 |
| 8 | 2.06 | 53.0 mv | .85 |
| 9 | 2.33 | 60.0 mv | .75 |

TABLE 2

The Maximum Oxide Film Resistances Measured

During the $Ag_2O \rightarrow AgO$ Plateau

| Number of Previous Cycles | [KOH] moles/$\ell$ | Charging Time (min) | Resistance Ohm·Cm$^2$ |
|---|---|---|---|
| 4 | 10.9 | 2.47 | <0.16 |
| 4 | 5.43 | 9.47 | 5.15 |
| 4 | 1.09 | 7.65 | 2.44 |
| 4 | 0.109 | 2.02 | 0.27 |
| 4 | 0.0543 | 1.48 | 0.31 |
| | | | |
| 0 | 1.09 | 2.34 | 0.35 |
| 1 | 1.09 | 3.29 | 0.97 |
| 2 | 1.09 | 3.96 | 1.51 |
| 3 | 1.09 | 4.32 | 2.09 |
| 4 | 1.09 | 4.58 | 2.14 |

Table 3

Charge Acceptance as a Function of Applied Potential

(Constant Through a Specific Oxidation)

| Potential (volts) | Electrode Type f = foil w = wire | Charge Acceptance per unit area (mcoul/cm$^2$) | Time Required to Reach Background (min) |
|---|---|---|---|
| .2785 | f | 1 | - |
| .2888 | f | 8 | - |
| .3004 | f | 28 | - |
| .3110 | f | 40 | - |
| .3155 | f | 106 | - |
| .3200 | f | 94 | - |
| .3230 | f | 114,114,106 | - |
| .3236 | f | 121,118,110,118 | 41 |
| .3310 | f | 129,137,141 | 46 |
| .3320 | f | 141 | - |
| .3384 | f | 143 | - |
| .3387 | f | 145 | 48 |
| .3402 | f | 117 | - |
| .3430 | f | 102,94,90 | - |
| .3610 | f | 86 | 18 |
| .3725 | f | 70 | - |
| .3842 | f | 62 | - |
| .4004 | f | 58 | - |
| .4126 | f | 63 | 12 |
| .4245 | f | 86 | - |
| .4414 | f | 94 | 13 |
| .4587 | f | 113 | - |
| .4688 | f | 117 | - |
| .4866 | w | 104 | 20 |
| .4880 | f | 113 | - |
| .4987 | f | 130 | - |
| .5079 | w | 100 | 30 |
| .5105 | f | 121 | - |
| .5109 | f | 102 | - |
| .5220 | f | 130 | - |
| .5317 | w | 119 | 28 |
| .5335 | f | 122 | - |
| .5547 | w | 130 | 37 |
| .5625 | w | 486 | 96 |
| .5743 | f | 471 | - |
| .5790 | f | 392 | - |
| .5845 | w | 127 | 11 |
| .5910 | f | 165 | - |
| .6016 | w | 71 | 4 |
| .6134 | w | 69 | 3.5 |
| .6335 | w | 99 | 8 |
| .6604 | w | 5557 | n.d.* |
| .71 | w or f | oxygen evolution | |

*After 180 minutes the current was still several times background current; therefore, not determined (n.d.).

Table 4

Charge Acceptance from (1) Current Integration and (2) Reduction at Constant Current in Region IV, Figure 8.

| Potential (volts) | Charge from Current Integration (mcoul/cm$^2$) | Charge from Reduction (mcoul/cm$^2$) | Time of Oxidation (min) | Time of First Reduction Plateau (min) | Time of Second Reduction Plateau (min) |
|---|---|---|---|---|---|
| 0.5625 | 486 | 372 | 96 | 0.21 | 2.27 |
| 0.5845 | 127 | 122 | 11 | 0.14 | 0.66 |
| 0.6016 | 71 | 69 | 4 | 0.05 | 0.42 |
| 0.6134 | 69 | 69 | 3.5 | 0.04 | 0.40 |
| 0.6375 | 99 | 90 | 8 | 0.10 | 0.50 |

- a -

- b -
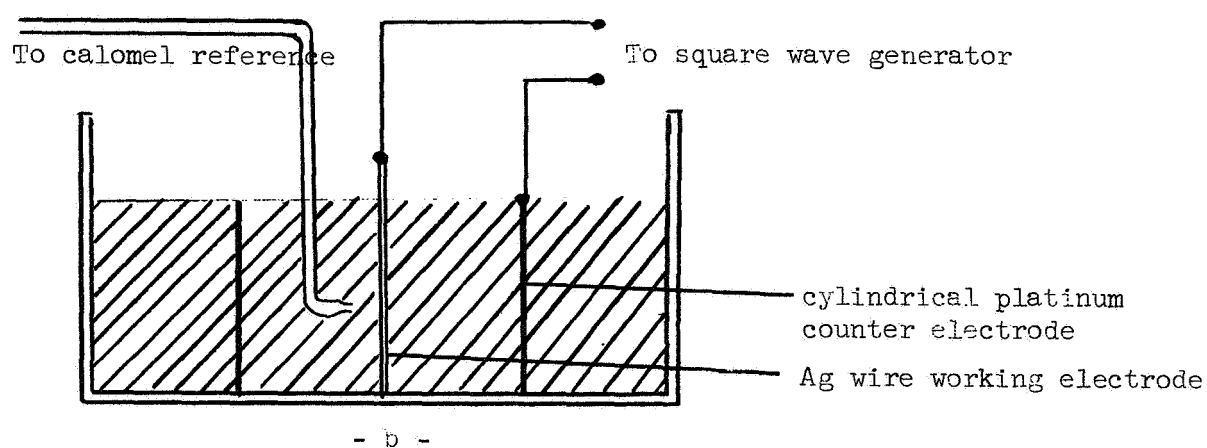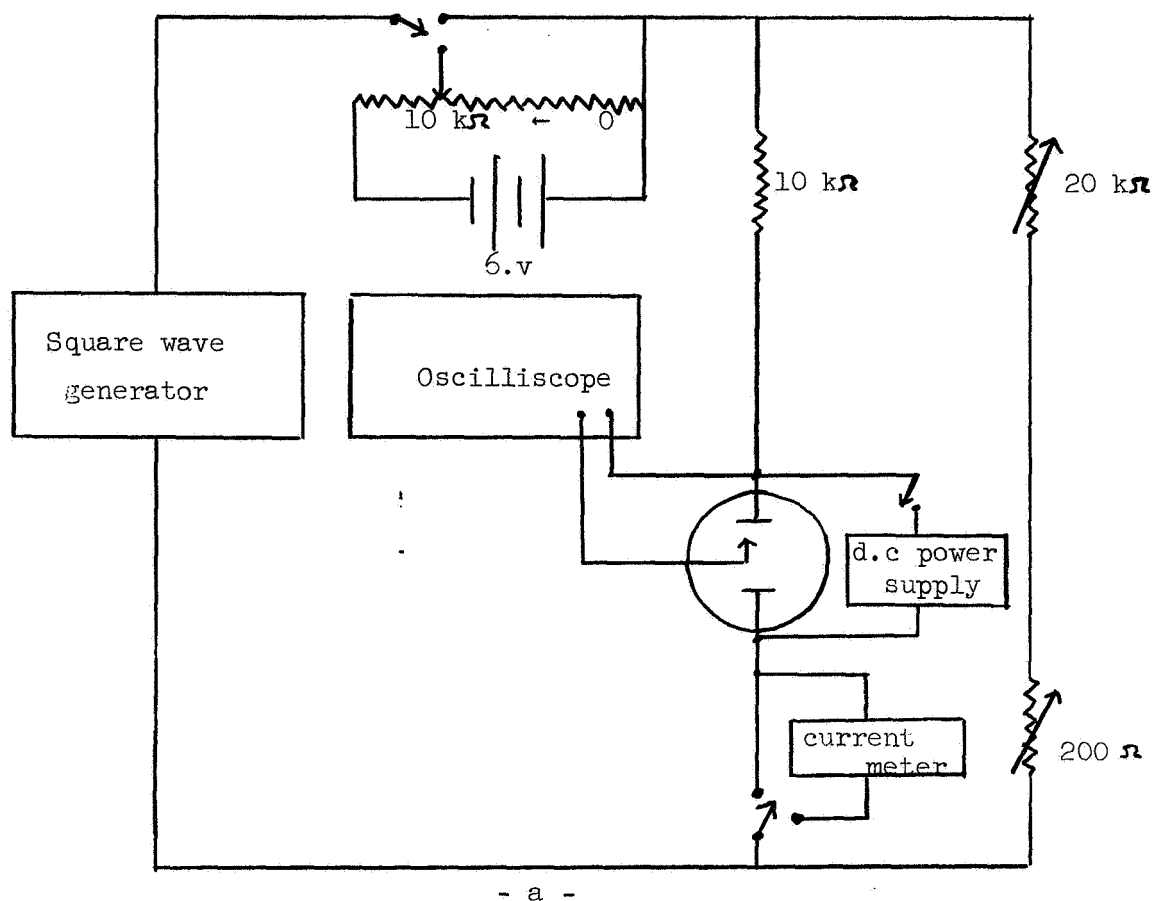
Fig. 1 . -- Modified c.c.s. apparatus.  a) circuit diagram
b) cell diagram.

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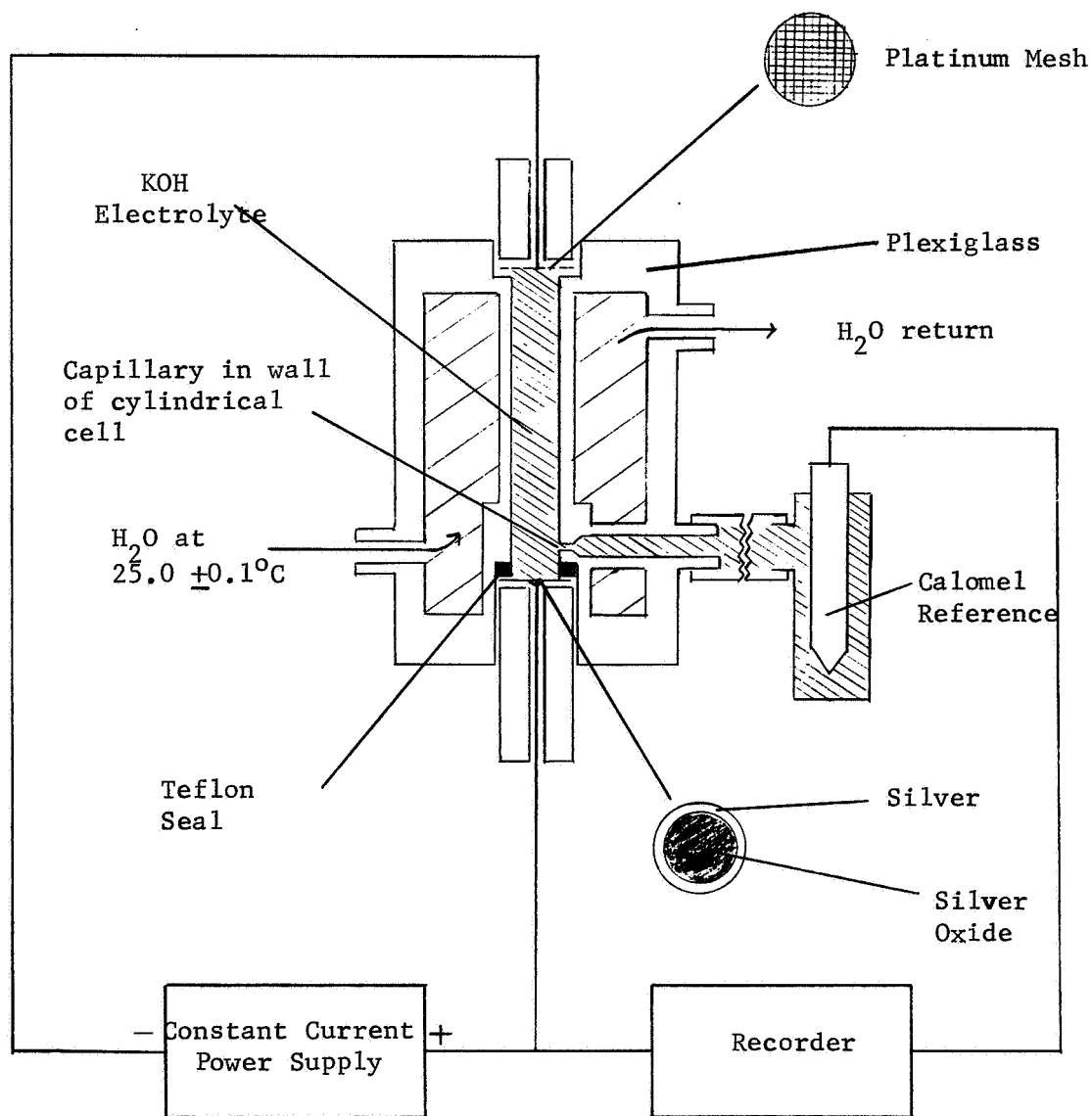


Fig. 2. -- Apparatus for charge acceptance data from which the values of the ratio $r = Q_{H}/Q_{total}$ were determined.
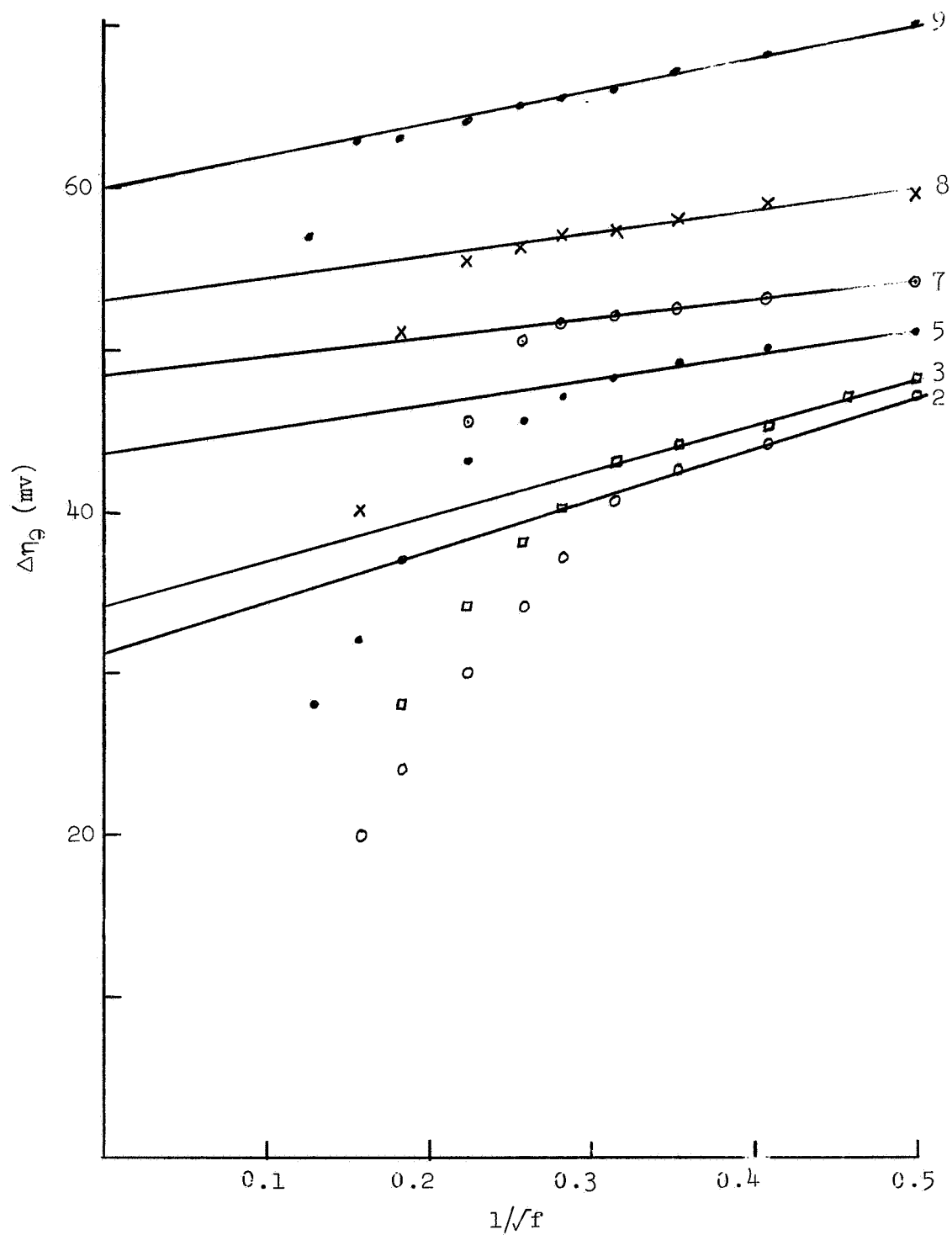
Fig. 3. -- Typical plots of c.c.s. measurements. The
numbers correspond to numbers given in Table 1.
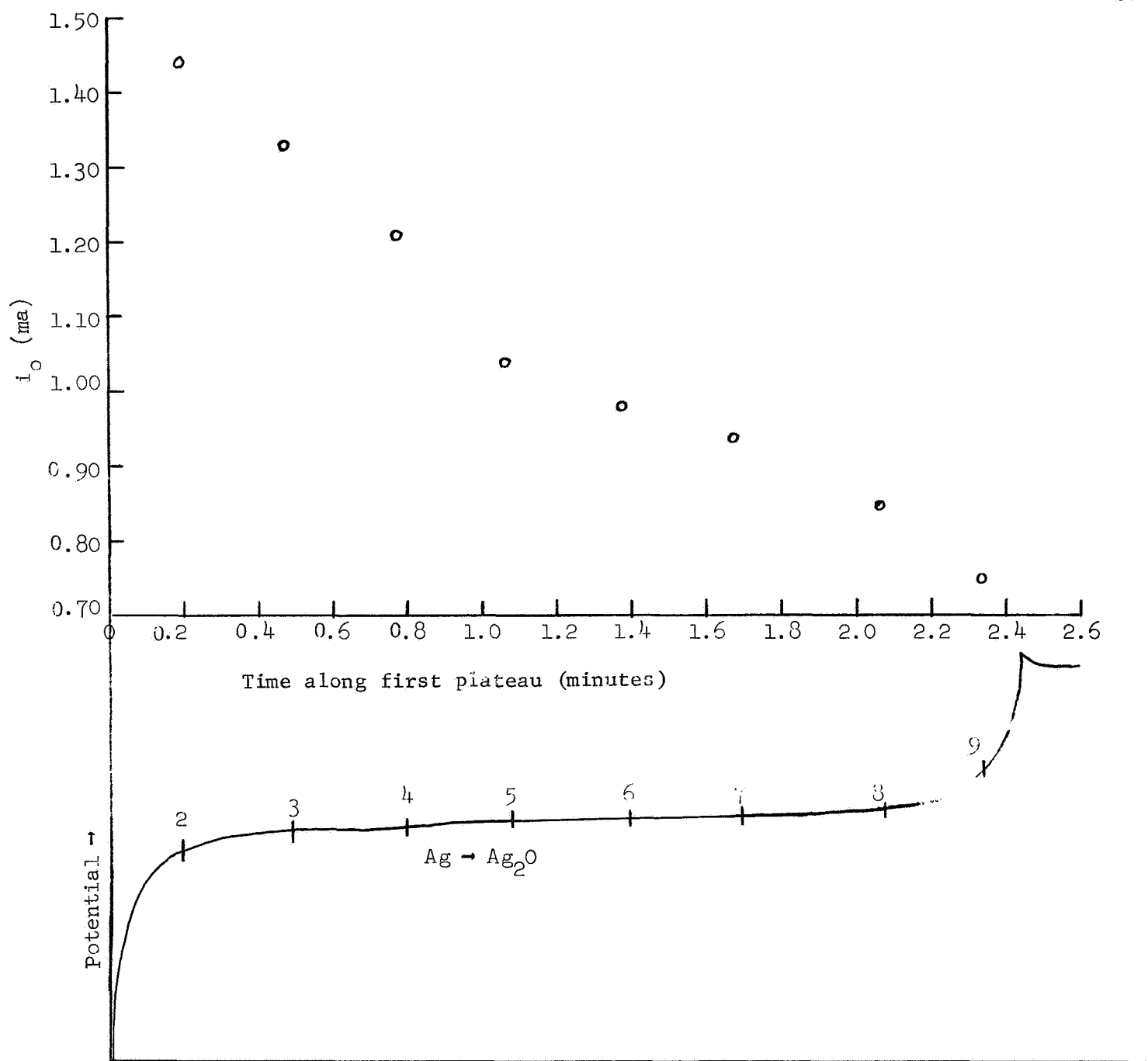
Fig. 4. -- Plot of $i_o$ versus time along first oxidation plateau, with corresponding points marked on the potential-time curve shown below. The numbers correspond to the run numbers in Table 1.
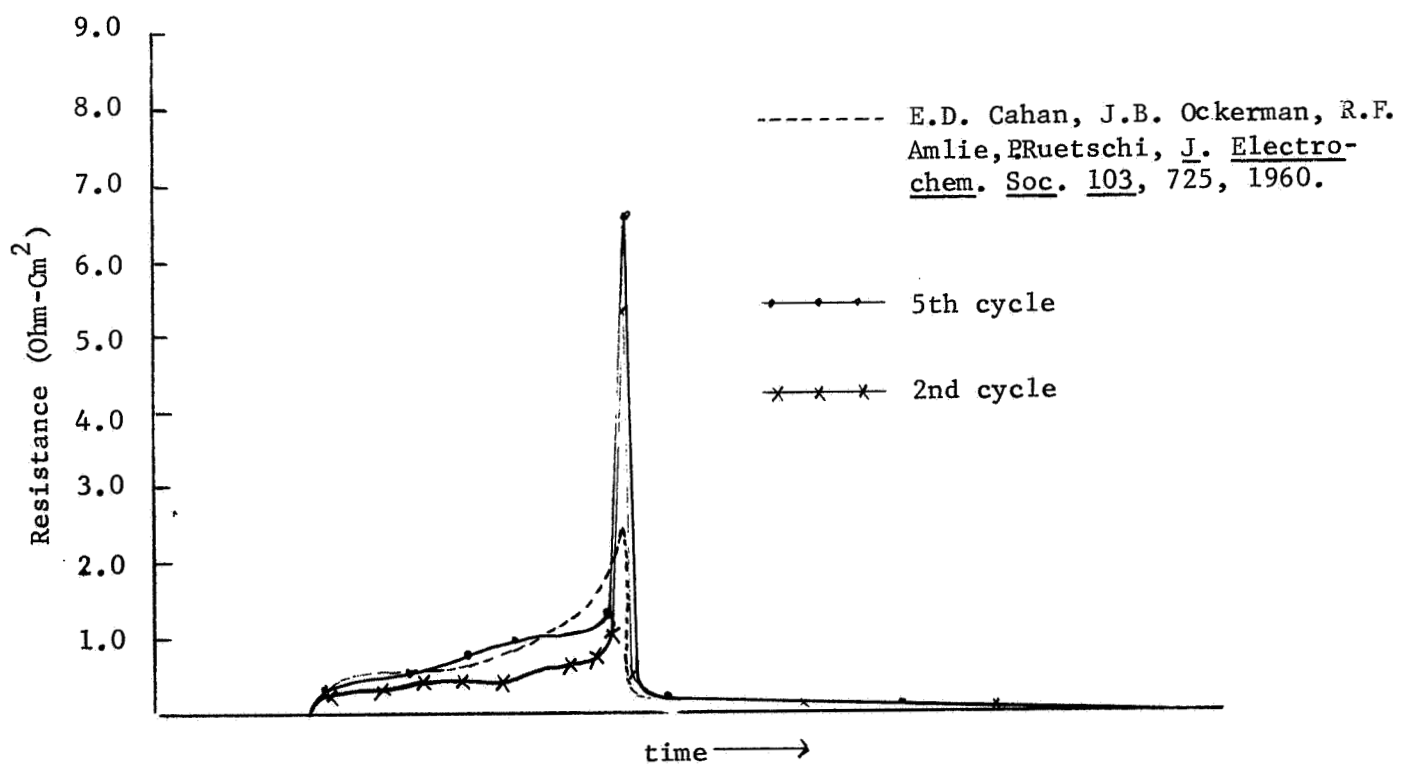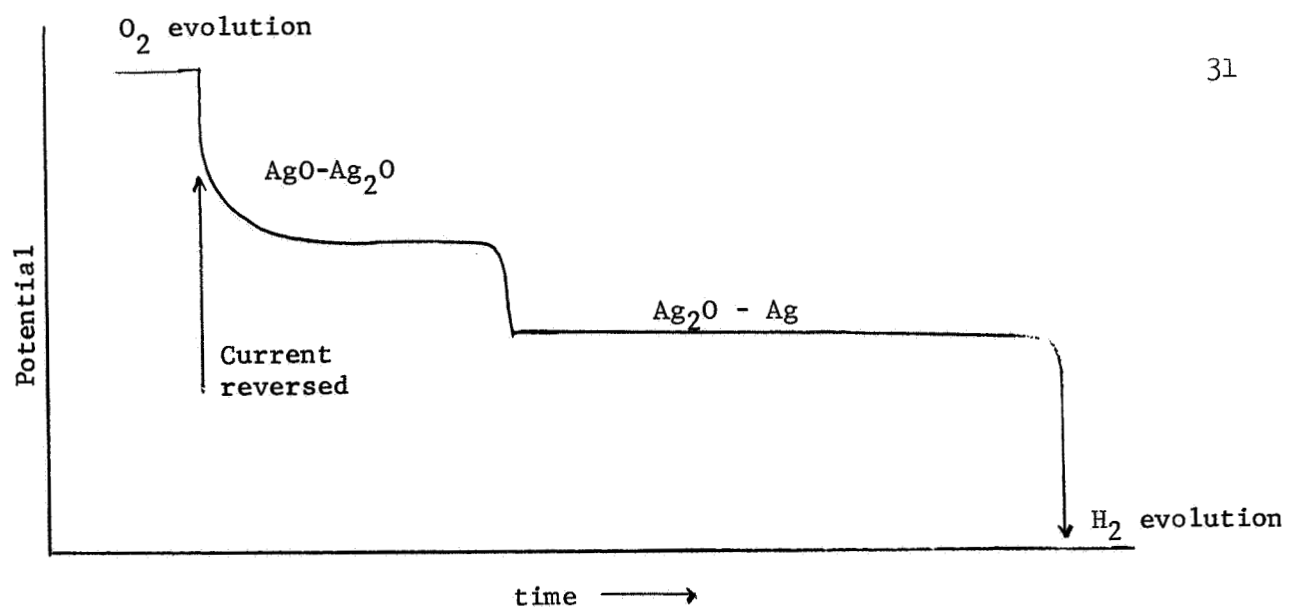
Fig. 5. -- Comparison of oxide layer resistance curves with potential time curve.
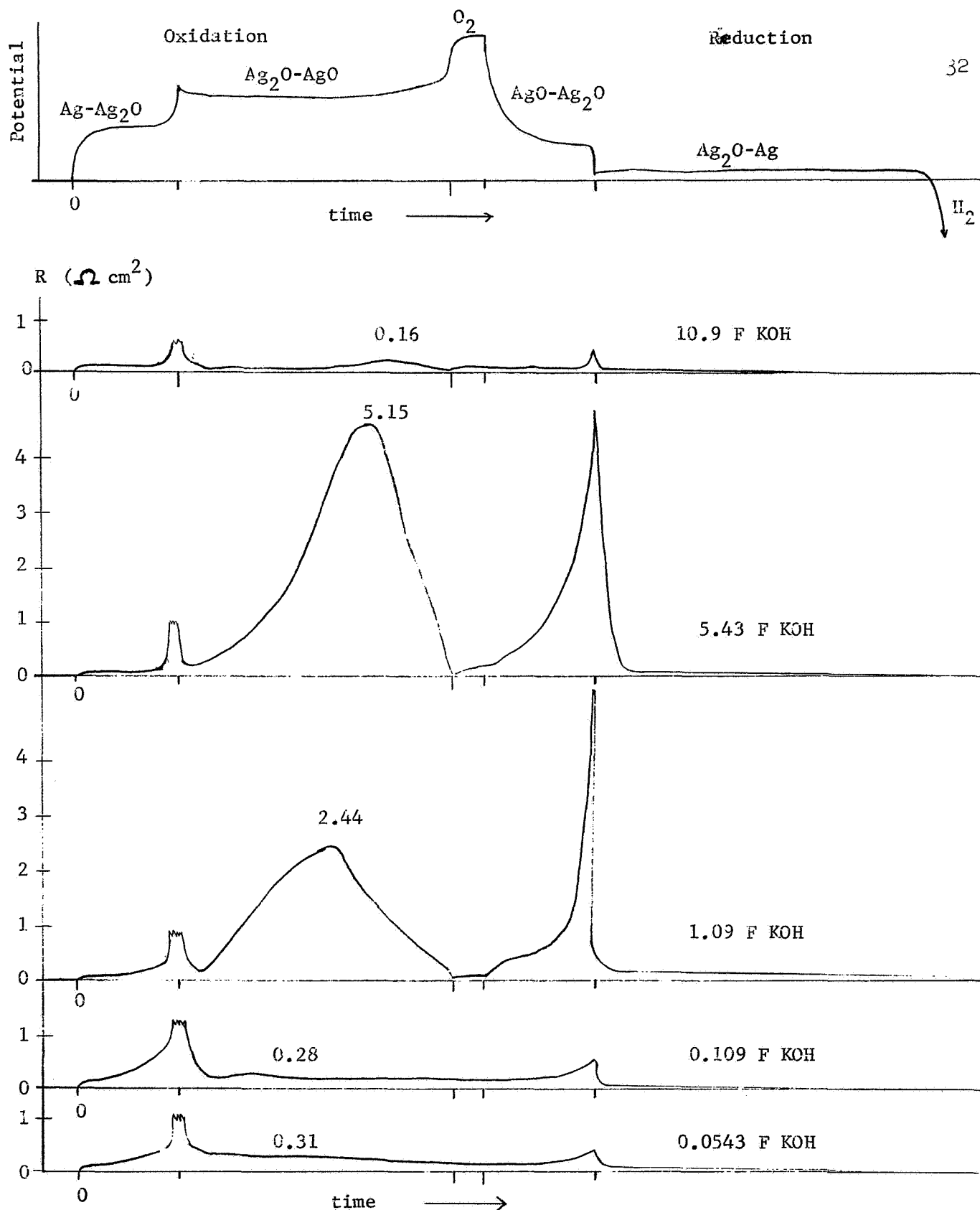
Fig. 6. -- The resistance versus time curves for the oxidation and reduction of silver in 10.9 - 0.543 F KOH. All resistance curves are normalized to the potential-time curve at the top.
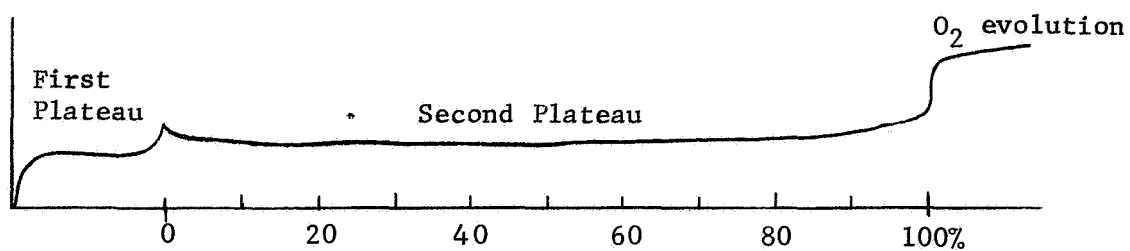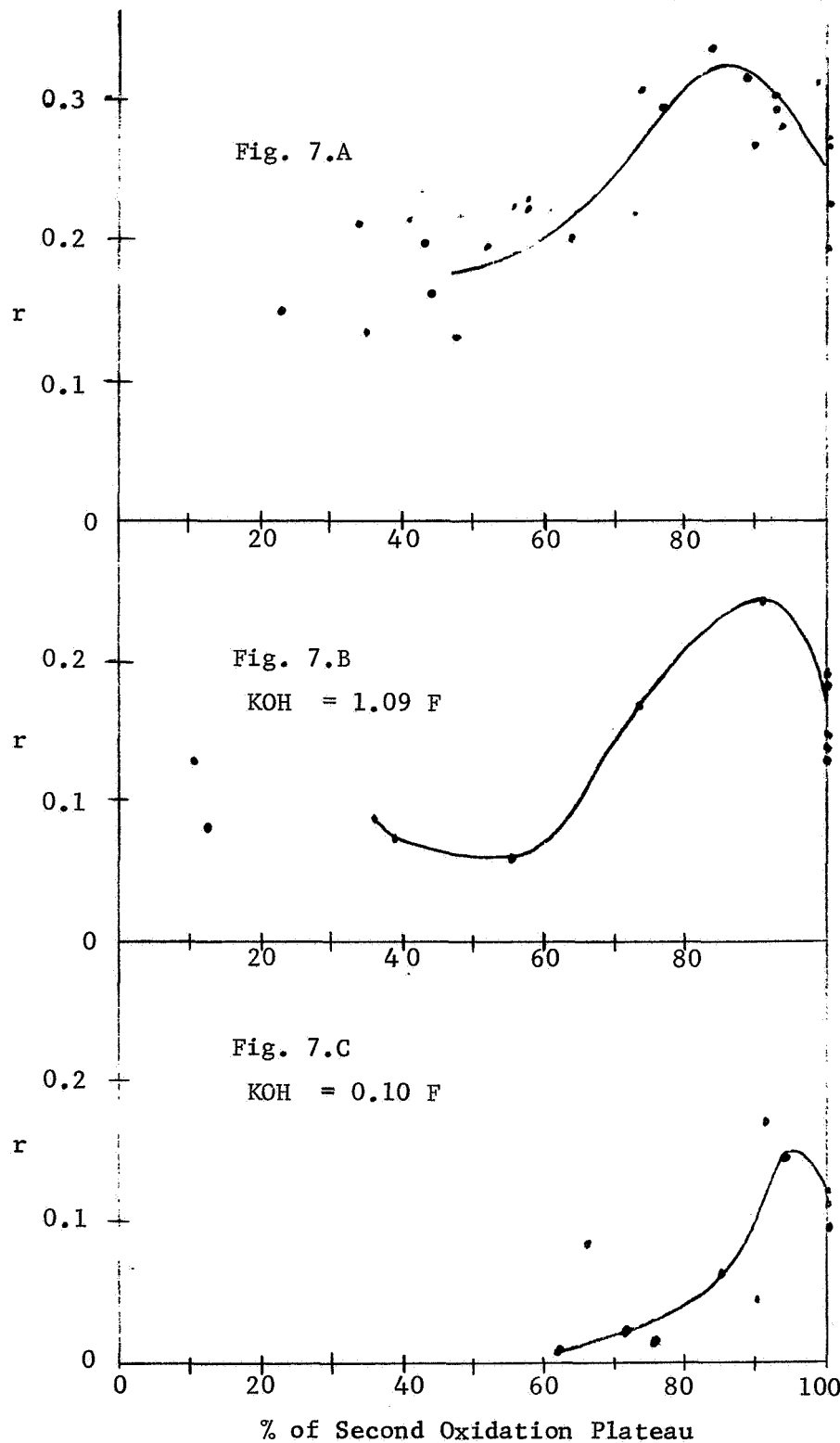
Fig. 7. -- The ratio, r, plotted against % of second plateau.
The 1.09 F KOH in A was reused in successive r
determinations and in B it was replaced after each
run.
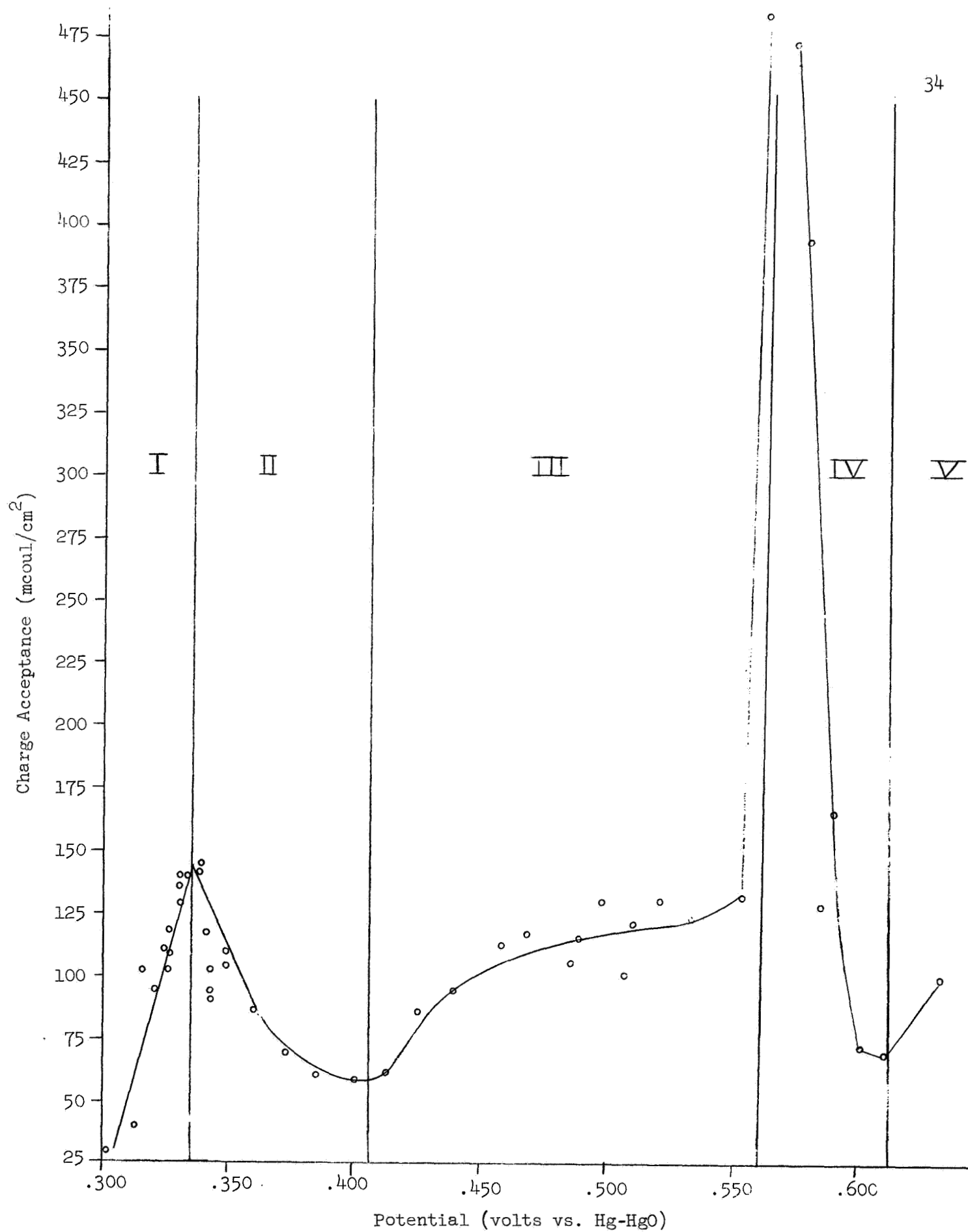
Fig. 8. -- Plot of charge acceptance per unit area versus applied potential. The plot was made using silver foil and wire electrode.
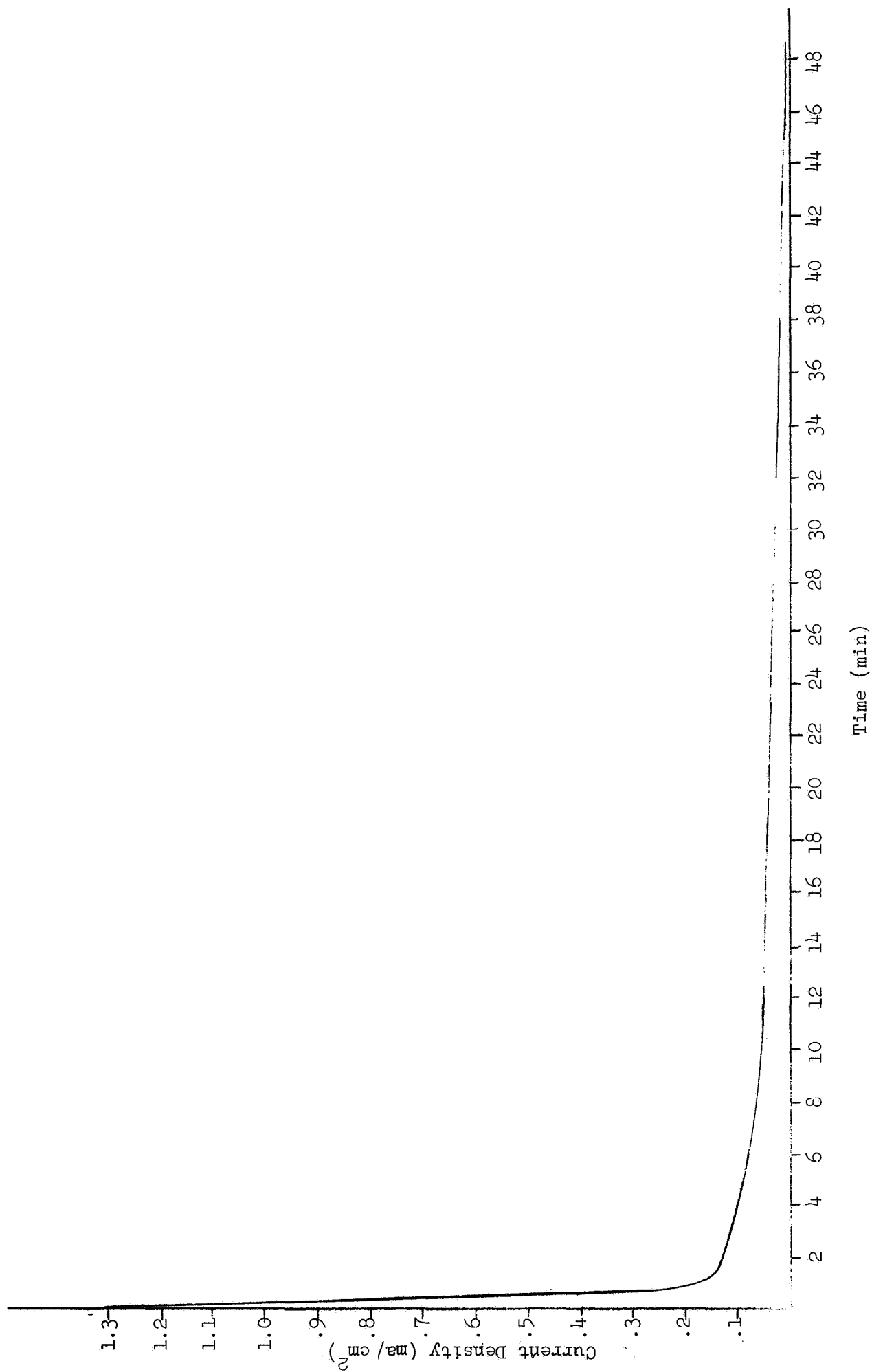
Figure 9. -- Plot from recording of current flow versus time for region I of Figure 8.  Potential 0.3310 volts (versus Hg-HgO)

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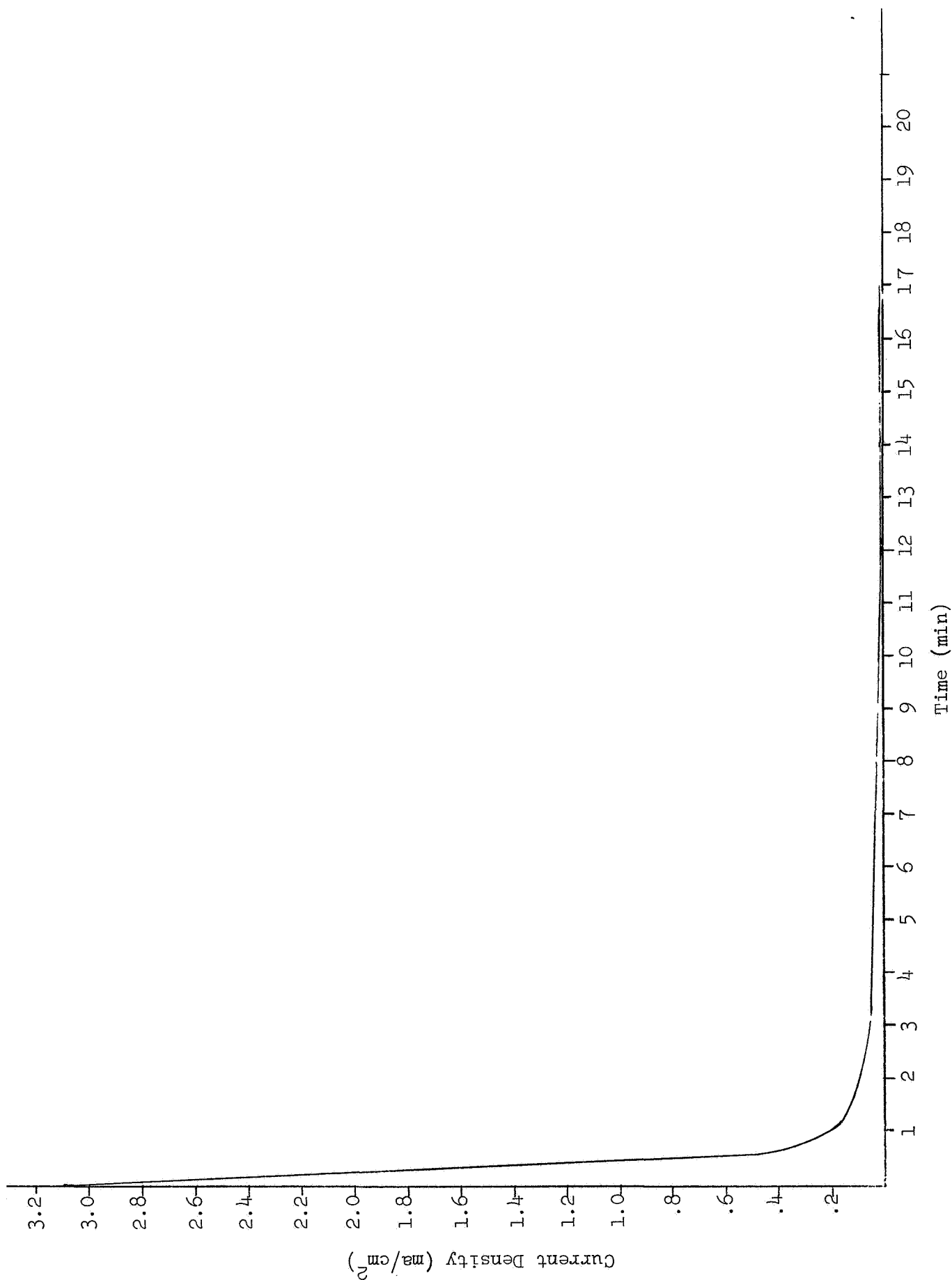
Figure 10. -- Plot from recording of current flow versus time for region II of Figure 8. Potential 0.4120 volts (versus Hg-HgO)
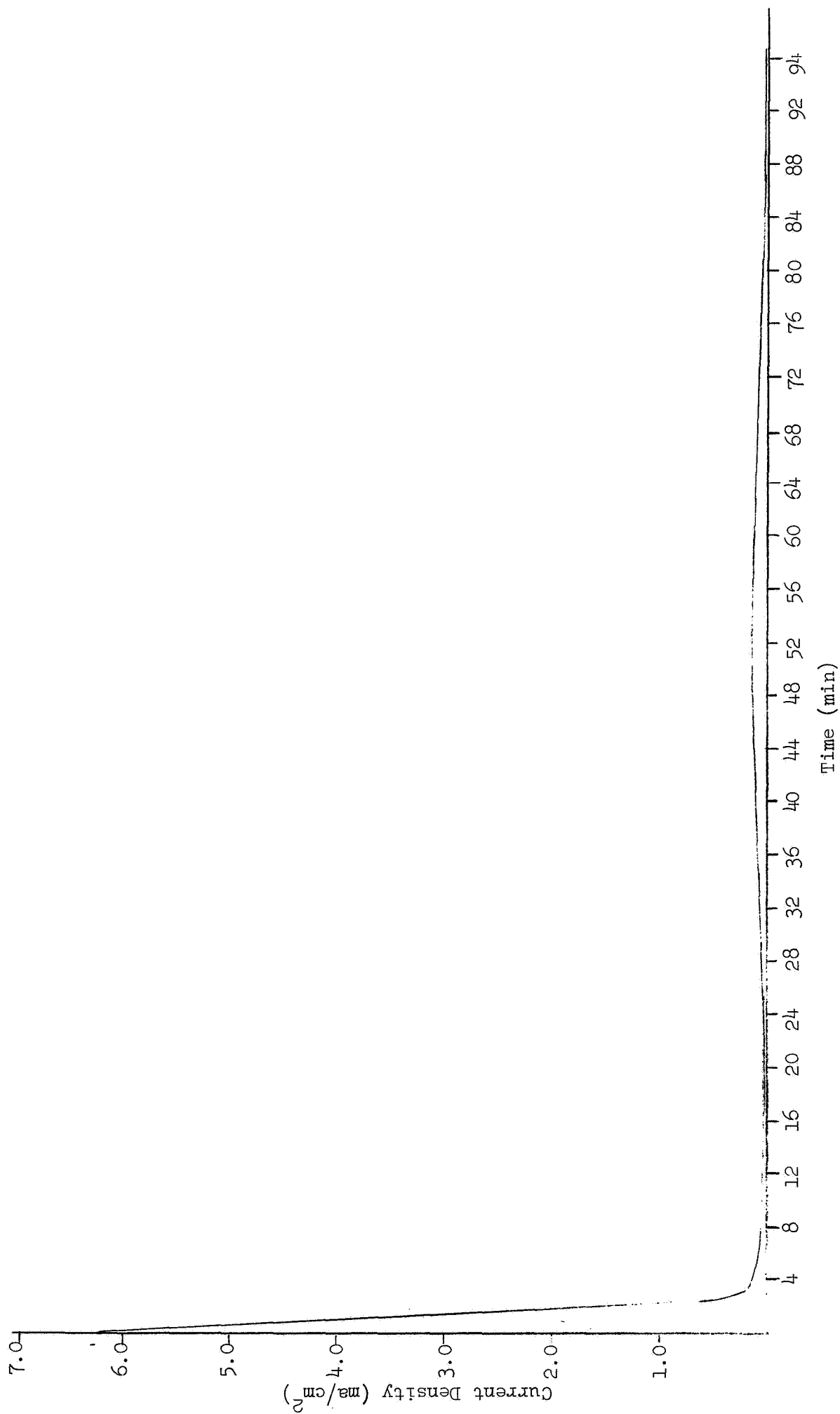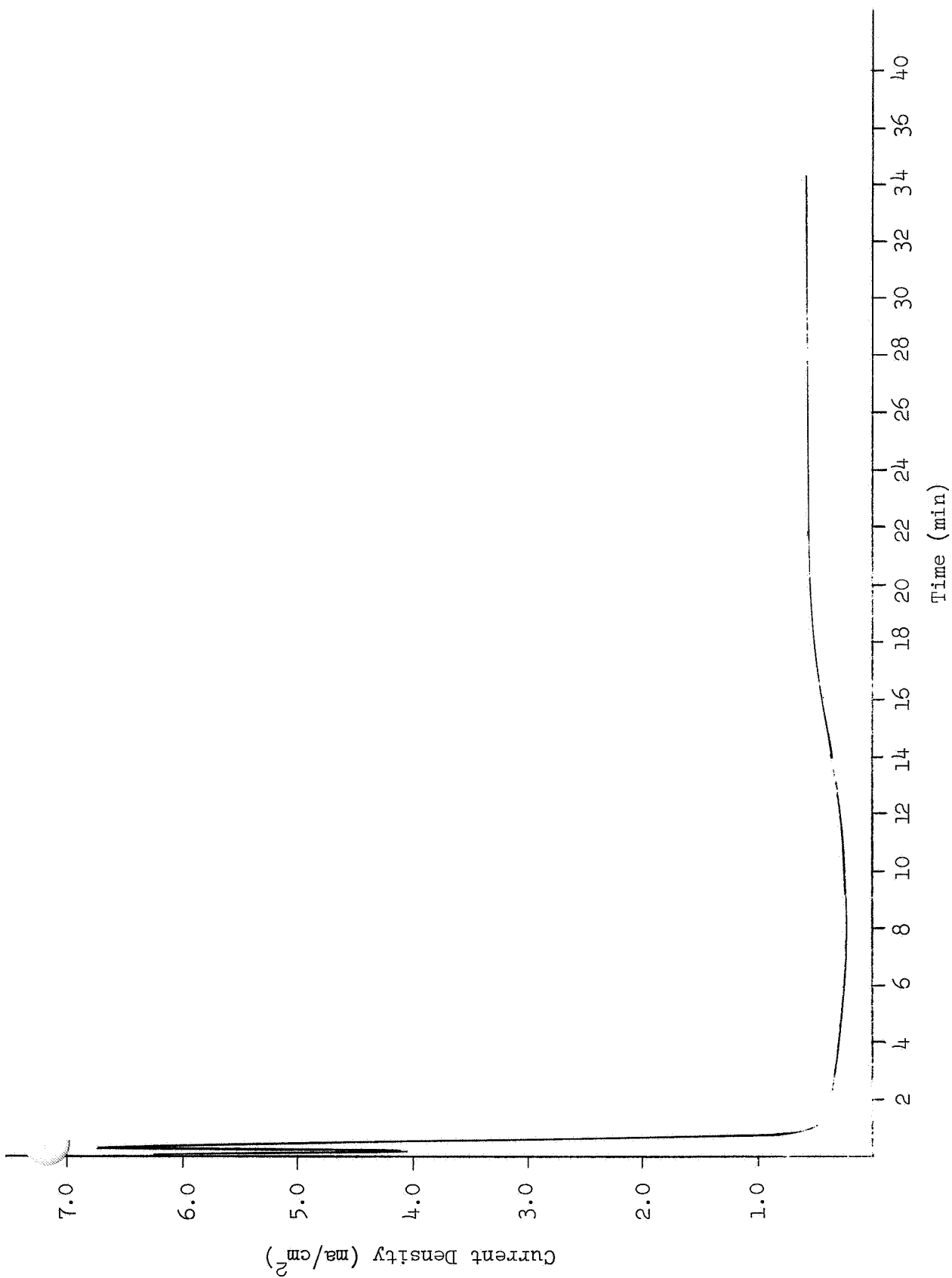
Figure 11. -- Plot from recording of current versus time for region III of Figure 8. Potential 0.5625 volts (versus Hg-HgO)
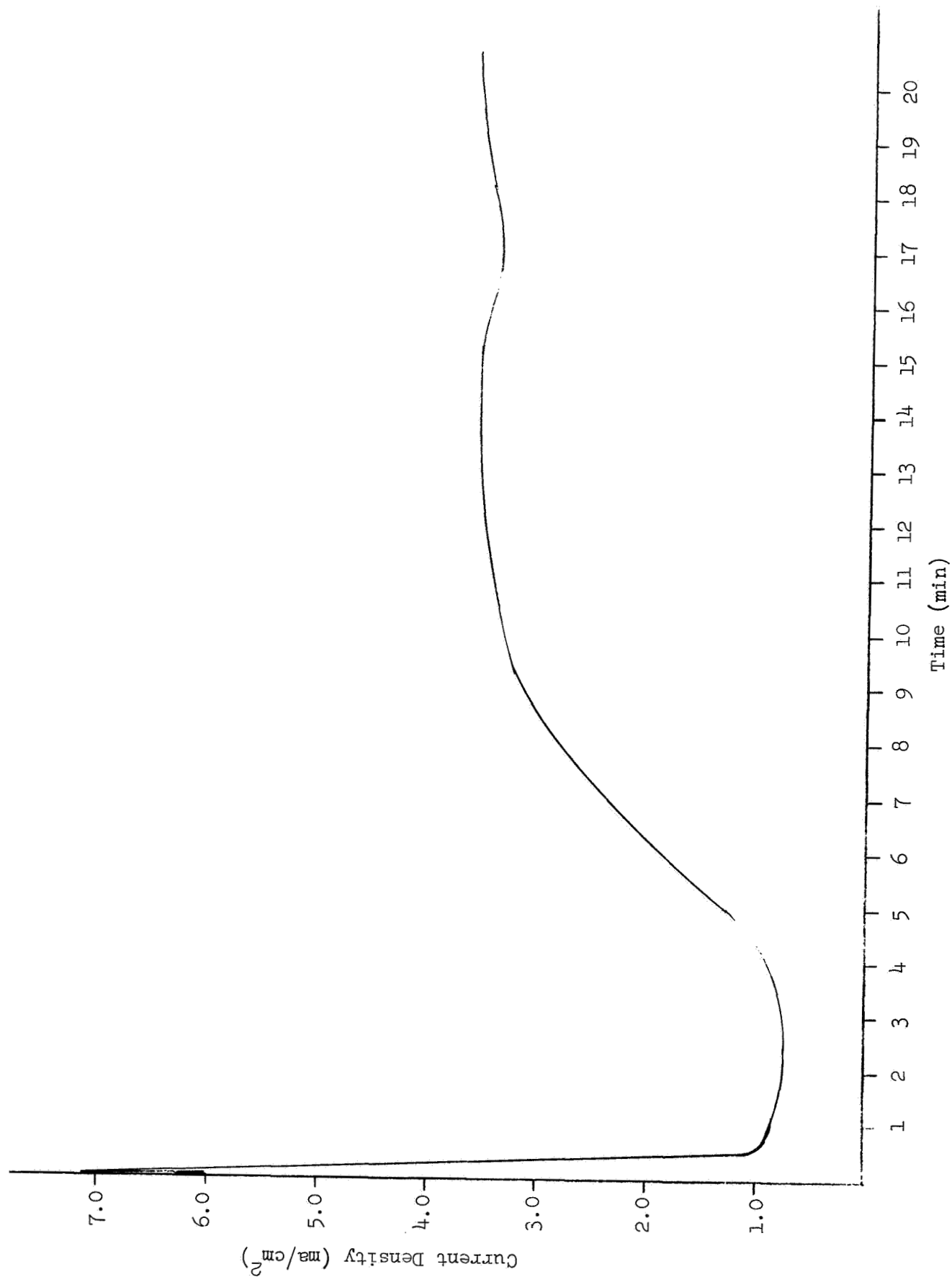
37
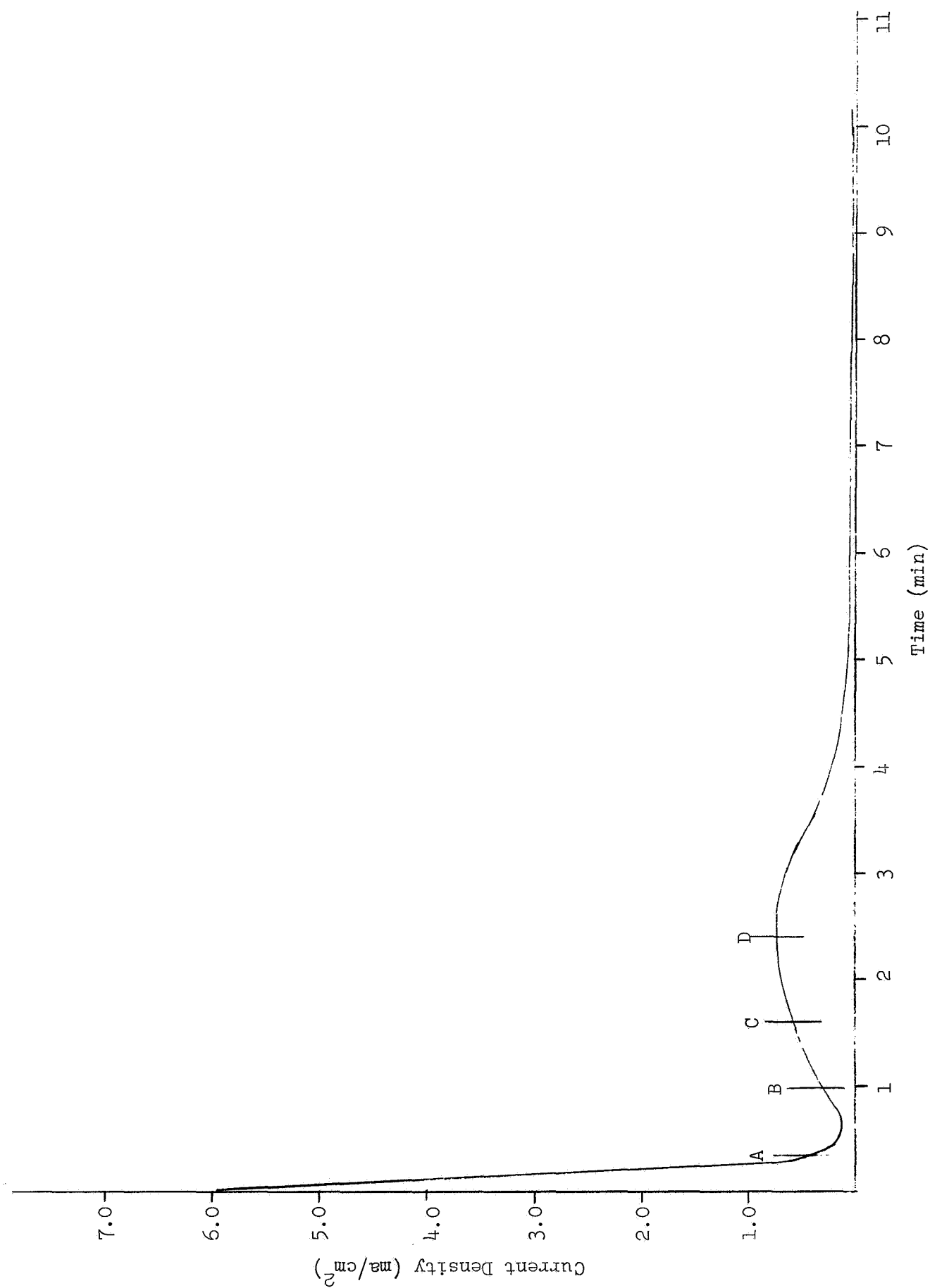
Figure 12. -- Plot from recording of current versus time for region IV of Figure 8. Points A, B, C and D represent points at which the oxidation was interrupted and the surface of the electrode was examined. Potential 0.5845 volts (versus Hg-HgO)

Figure 13. -- Plot from recording of current versus time for region V of Figure 8. Potential 0.6606 volts (versus Hg-HgO)

Figure 14. -- Plot from recording of current versus time for region V of figure 8. Oxygen evolution was noted at this potential. Potential 0.7126 volts (versus Hg-HgO)
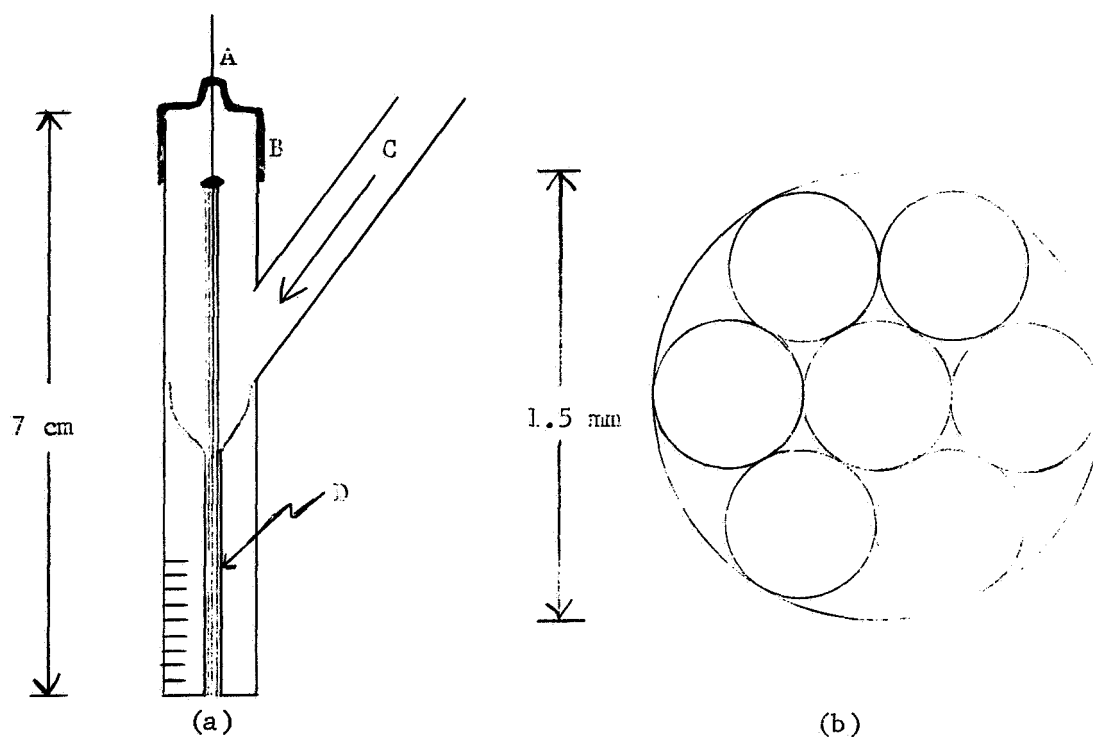
Fig. 15. -- (a) Model pore capillary electrode (side view)
(b) End view of model pore showing arrangement of
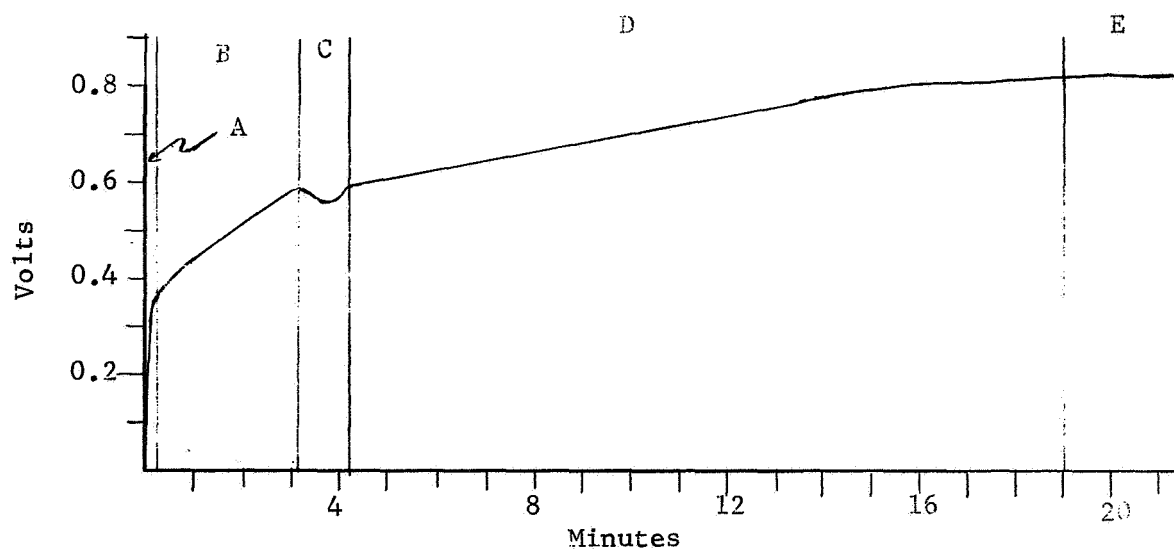silver wires within the capillary.



Fig. 16. -- Potential-time curve for oxidation in a model pore
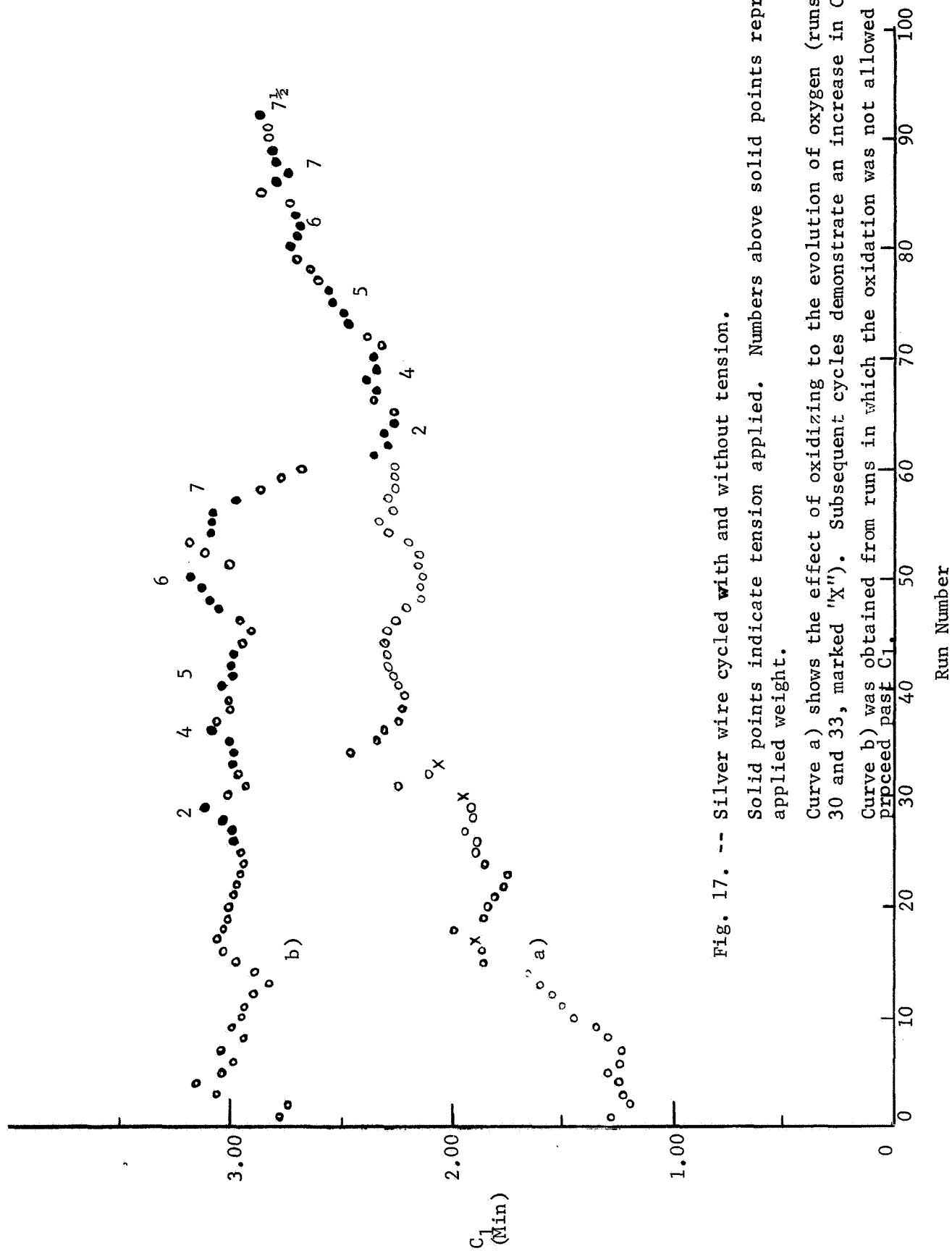electrode. Current = 160 μamp.

Fig. 17. -- Silver wire cycled with and without tension.

Solid points indicate tension applied. Numbers above solid points represent applied weight.

Curve a) shows the effect of oxidizing to the evolution of oxygen (runs 17, 30 and 33, marked "X"). Subsequent cycles demonstrate an increase in $C_1$.

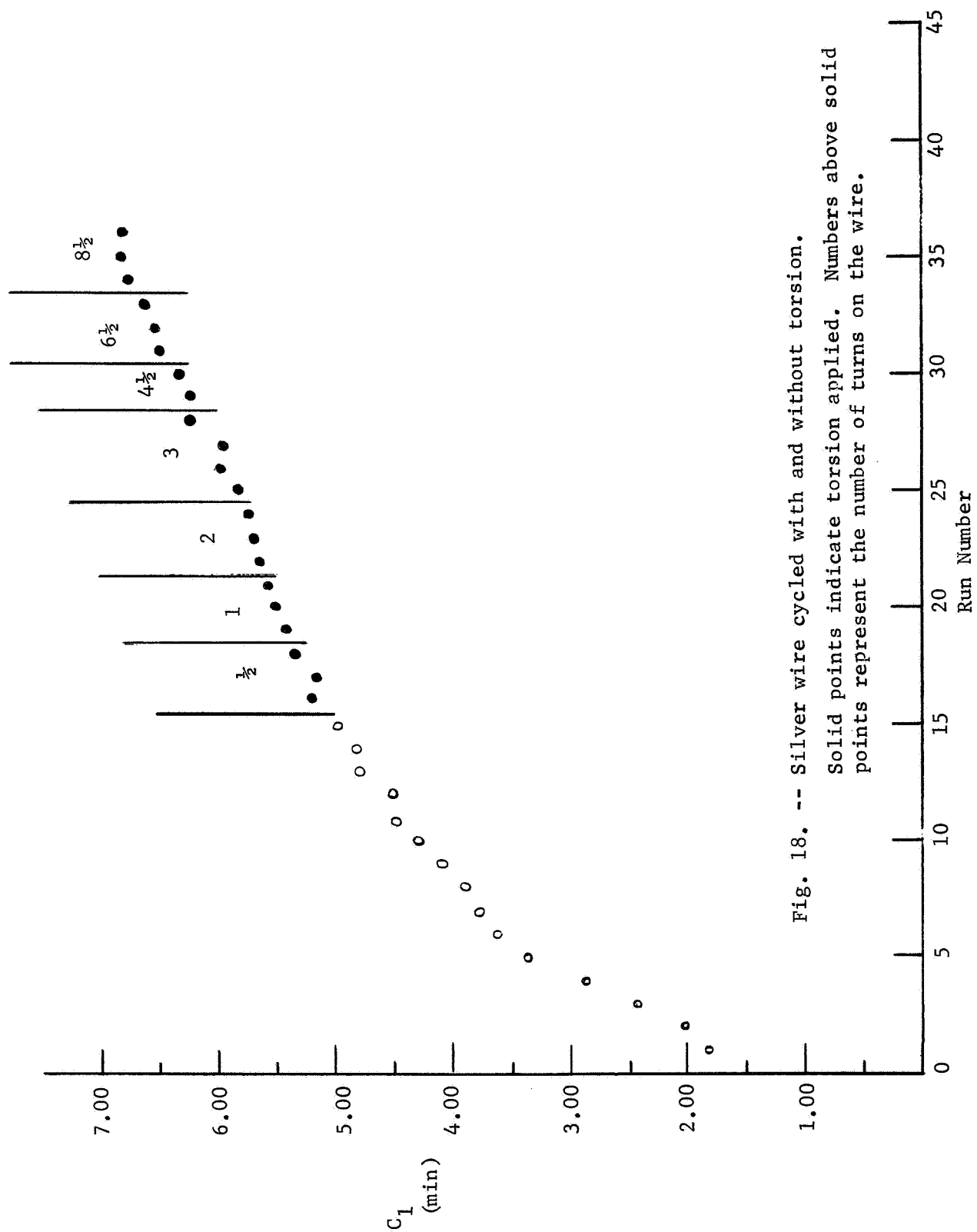Curve b) was obtained from runs in which the oxidation was not allowed to proceed past $C_1$.

Fig. 18. -- Silver wire cycled with and without torsion. Numbers above solid
points indicate torsion applied. Numbers above solid
points represent the number of turns on the wire.

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